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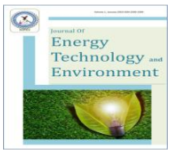

# Optimum biodiesel production from waste vegetable oil using functionalized cockle shell and watermelon peels as catalyst

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## Abstract

*The components of bio-waste are particularly abundant in essential minerals like calcium and potassium, which are essential for the manufacture of high-performance biocatalysts for biodiesel synthesis. This research evaluated the prospect of bio-waste heterogeneous catalyst of fused cockle shells and watermelon peels to transesterify waste vegetable oil. At 900°C and 500°C, the waste feedstocks were dried, calcined, and carbonized, respectively. In order to evaluate the compositional, morphological, structural, and thermal features of both the precursor material as well as the catalyst, they were both characterized. The Box-Behnken design was employed to generate 29 experimental runs to investigate the impact of operational variables notably reaction time, catalyst loading, temperature, and methanol-to-oil molar ratio. The existence of acidic oxides (nickel and silicon) as well as basic oxides (potassium and calcium) demonstrated that the synthesized catalyst was bi-functional. The catalyst's surface area (105.35 $m^2/g$) and pore volume (0.60 $cm^3/g$) obtained from the BET analysis contributed to a 91.77% biodiesel yield at 63.34 °C reaction temperature, 149.41 min reaction time, 1.05wt% catalyst loading, and a 14.45:1 methanol to oil ratio. The physicochemical parameters of the biodiesel produced were measured and determined to be acceptable in accordance with the European National (EN) and American Society for Testing of Materials (ASTM) quality standards, demonstrating the product's suitability for use as fuel*

## 1. Introduction

Energy is a necessity for human survival on a fundamental level. Because of the ever-increasing global population, the transportation, industrial, and power generation sectors consume the majority of global energy[1]. Currently, traditional fossil fuels including diesel fuel, natural gas, gasoline and liquefied petroleum gas provide the majority of energy. These fossil fuels and oil reserves are being depleted at an alarming rate, and its utilization has been identified to be a significant contributor to the discharge of hazardous gases [2]. To fulfill present and future energy demands, curb imminent problems and ecological effects, researchers began to investigate alternative sources [3]. For reducing the reliance on petroleum, biodiesel is a viable alternative among the various renewable energy sources. The use of biodiesel is a greener alternative to gasoline because it is nontoxic, biodegradable, carbon neutral, low-polluting, and environmentally beneficial [4]. Due to its chemical composition, biodiesel is an excellent substitute for regular diesel fuel [5].

Biodiesel is a renewable energy source for internal combustion engines made up of monoalkyl esters and long-chain fatty acids generated from biomass. In the process of producing biodiesel, a transesterification reaction is carried out with the primary lipid sources being animal fats, and algal oils. Additionally, alcohols and catalysts are utilized in the production process. In comparison to petroleum-based fuel, biodiesel becomes more expensive. It turns out that about 75% of the cost of making biodiesel fuel comes from the feedstock used [6]. This is because biodiesel is made from high-quality virgin oils like cottonseed, soybean, olive, sunflower and linseed. Biodiesel's production costs continue to be the main impediment to its widespread adoption as a fossil fuel replacement.

The utilization of low-quality feedstock like used vegetable oil (UVO) and non-edible oils in biodiesel synthesis is becoming more prevalent as a result of increase in food costs and environmental concerns. These oils are renewable and widely available, making their usage as feedstock for biodiesel synthesis economically viable [7]. Biodiesel production has a significant financial impact, so the catalyst employed is an important consideration. In this regard, the use of inexpensive and catalytically active solids with high efficiency may be the best course of action to take [8]. In contrast to liquid catalysts, which must be separated, purified, and ecofriendly before they can be used, solid catalysts have recently gained a lot of study focus as they are resistant to corrosion, can be reused and can be saponified. Due to the benefits they provide, they have recently been the focus of a lot of study [9].

Using waste to provide feedstock as catalyst for the reaction is one way to reduce biodiesel production costs while also reducing pollution and improving global health. In order to produce biodiesel from heterogeneous catalysts, many researchers have used a variety of precursor materials. For example [10], utilized waste cockle shell as a naturally occurring catalyst in the generation of biodiesel using a catalyst concentration of 1.5 wt%, a yield of 93.20 percent was achieved. [11] produced ash generating biodiesel from the peels of ripe plantain fruits as an environmentally friendly catalyst. They reported the biodiesel production utilizing plantain peels as a cheap feedstock. Despite the fact that heterogeneous catalysts based on calcium are more efficient, economical, and advantageous to the biodiesel production process, side reactions are possible in conjunction with the methanolysis process examples include the catalytic neutralization of free fatty acids and the saponification of glyceride and methyl ester, prolonged reaction times and catalyst efficiency decline due to active phase leaching into the reaction mixture.

Various strategies have been developed by researchers to combat this problem. For instance,[12] used $CaO$-$La_2O_3$ mixed oxide catalyst in biodiesel production from Jatropha Oil and obtained a yield of 98.76%. In spite of these results, it has been reported that metal oxide-based catalysts due to the small amount of surface area they possess, have a restricted capacity for the transmission of mass and reusability [13]. Some authors have combined biomass and calcium-based materials to create more active catalyst in order to overcome this challenge. In the context of heterogeneous catalyst production and subsequent application in transesterification reactions, a number of agricultural biomass wastes such as banana peduncle [14], cocoa pod husk [15], mango peels [16]have been employed.

The production of biodiesel is a multivariate process reliant on numerous variables. Several parameters, in particular, have been considered to maximize biodiesel yield. Multiple process variables, such as catalyst type/amount, reaction time, alcohol/oil ratio, and temperature, have been reported to have an impact on its performance. Tools for efficient modeling, such as the response surface method (RSM), is employed to examine the impact of the interaction variables and to establish the relation between the parameters and the response in order to ascertain the optimum operating conditions. Biodiesel production process design utilizes response surface methodology to reduce the number of experiments needed to optimize for efficiency in terms of time, cost, and other resources [17]. [18] in her work, reported optimal biodiesel production from mango seed oil utilizing transesterification reaction. RSM based optimization method was employed for the process parameters. The transesterification process utilized yielded a maximum of 95% biodiesel demonstrating the potential of mango seed oil as a feedstock for the synthesis of biodiesel, hence, advancing the field of renewable energy. This study, highlights the need for a cleaner energy via biodiesel production.

Considering biodiesel as the most effective alternative to fossil fuel, [19] in their study, generated biodiesel from used frying oil via transesterification reaction attaining a maximum yield of 95.87% to 97.34%. A 9:1 molar ratio of methanol to used frying oil, reaction temperature of 60°C,1.5% KOH by weight of oil, and an agitation intensity of 600 rpm were determined to be the ideal parameters for producing biodiesel. The oil conversion process into biodiesel was verified by GCMS and FTIR analysis. Through their research, they demonstrated the potential of biodiesel as a feasible fuel source for applications in diesel engines, hence helping to mitigate the world's growing fuel demand.

With biodiesel being a reliable substitute for non-renewable energy, [20] carried out a sustainable production of biodiesel from waste frying oil using banana peels and egg shells modified with ZnO. Important process variables such reaction temperature, methanol-to-oil ratio, and catalyst loading were employed in order to optimize the catalyst's reaction characteristics both before and after modification. A statistical analysis was performed on the data with a 95% yield level of biodiesel utilizing a wet impregnation approach while adopting the transesterification process of the purified oil using $CaO/K_2O\text{-}ZnO$ catalyst. Through physicochemical analysis, the quality of the biodiesel produced was verified.

Optimizing biodiesel production by synthesizing a heterogeneous bio-based catalyst from waste cockle shells and watermelon peels is the focus of this study, which aims to advance research toward a more cost-effective, ecologically friendly biodiesel production process using waste vegetable oil. To improve its characteristics, doping the catalyst with nickel nitrate boosted its functionality. Utilizing RSM, the production process was optimized and modelled. To the best of our knowledge, biodiesel production from used vegetable oil using fused cockle shell and watermelon peel for the development of heterogeneous catalysts have not been investigated, thus the need for this research.

## 2. Materials and Methods

### 2.1 Materials

The utilized used vegetable oil (UVO) was sourced from the University of Benin, Edo state, Nigeria Canteen. The cockle shells and watermelon peels utilized in the catalyst synthesis process were sourced from Borokiri market in Port Harcourt and a local retailer in Benin, Nigeria respectively. The chemical reagents, benzene, ethanol, methanol, potassium iodide, potassium hydroxide, acetic acid, hydrochloric acid, nickel nitrate employed in this study was of analytical standard and obtained from the Chemical Engineering Laboratory, University of Benin.

### 2.2 Preparation of the Catalyst

The cockle shells was given a thorough hot water wash to help remove proteins and lipids, afterwards washed in distilled water to remove any dust and debris left before being sun dried for about 3 days. A powdered form of the cockle shell was obtained by crushing the shells in a laboratory mill and sieving them through a sieve tray with a size of 300μm. In a muffle furnace, the powdered cockle shell was calcinated for four hours at a temperature of 900°C. To avoid air contact, the calcined cockle shell was removed after cooling and immediately placed in a desiccator. The acquired watermelon peels was prepared in same method, the watermelon peels was separated from unwanted debris and dirt by washing thoroughly with distilled water, chopped into pieces, and dried under the sun for 4 days. A powdered form of the watermelon peels was obtained by crushing the peels in a laboratory mill and sieving them through a sieve tray with a size of 300µm. For three hours at 500°C in a muffle furnace, powdered watermelon peels were carbonized. The calcined watermelon peel ash samples that were produced were kept in a desiccator until they could be used for further testing. The wet impregnation technique was utilized for the preparation of the nickel-doped composite catalyst from carbonized watermelon peels and calcined cockle shell, as reported by [21]. Mixed in proportions of 70% (calcined cockle shell), 17% (carbonized watermelon peels), and 13% (nickel nitrate), and dissolved with 400ml of deionized water. The mixture was agitated continuously for 2hours using a magnetic stirrer hotplate at 80°C. The ensuing slurry was initially dried in an oven for 1 hour before being subjected to a 4-hour heat treatment in a muffle furnace at 900°C. Manually, using a porcelain mortar and pestle, the calcined slurry was crushed into fine particulates. The synthesized catalyst was cooled in a desiccator and subsequently stored in an airtight canister for further analysis.

### 2.3 Characterization of Catalyst

With the intent of evaluating the characteristics of the newly synthesized catalyst (cockle shell and watermelon peels) as well as its precursors, various characterization tests were run on the samples. The surface morphology and elemental composition of the catalyst and precursor materials were determined using the Scanning Electron Microscopy which utilizes an energy dispersive X-ray detector (SEM)-EDX technique. An X-ray diffractometer (XRD) with Cu Kα radiation was utilized to examine the catalysts' crystalline phase. The developed fused catalyst was subjected to the Brunauer, Emmett and Teller (BET) and Barrett-Joyner-Halenda (BJH) analysis used to determine the surface area and pore volume. Fourier Transform Infrared Spectroscopy (FTIR) analysis was utilized to determine the bond structure and interactions in the calcined catalyst at a resolution of 4cm$^{-1}$ examined at a spectra range between 4000 and 400 cm$^{-1}$ using the Pelkin Elmer 3000MX spectrometer.

### 2.4 Experimental design and RSM modelling

Response surface methodology, a flexible mathematical tool was employed for parametric modelling and design of the transesterification process [22]. Design Expert Software was employed in this study to conduct experimental runs and optimization of reaction conditions. The parameters for inputs were established through preliminary experimentation and prior research. The process of transesterification was modeled and optimized utilizing the BBD with three factors and three levels. Twenty-nine experimental runs with a single response were produced. The Box-Benhken (BBD) tool in the STATISTICA 10 software was employed for experimental design using the following ranges of experimental values as shown in the table 1. Table 1 shows the coded and actual levels of the independent variables. The analysis of variance (ANOVA) is used to assess the model's goodness of fit and the key process variables that influence the production of biodiesel. The fitness of the model is described in Equation 1.

$$aY = \beta_o + \sum_{i=1}^{k} \boldsymbol{\beta_i X_i} + \sum_{i=1}^{k} \boldsymbol{\beta_{ii} X_{ii}^2} + \sum_{i<j} \sum \boldsymbol{\beta_{ij}} \ \boldsymbol{X_i X_j} + \varepsilon \qquad (1)$$

Where Y represents the output, βo denotes the intercept, βi represents the slope or linear effect of the input variable Xi, βij the linear by linear interaction impact between the input variables Xi and Xj, βii is the quadratic influence of input variables, ε is random error.

Based on the selected model parameter such as F value, lack of fit, p value etc., ANOVA results estimate the statistical significance and fit of a model, which can be tested by comparing variations in the model's explanations and in the model's residuals.

Table 1: Process Variable and their Lower, Middle and Upper Bounds

| Process Variables | Symbol | Coded and actual levels | | |
|---|---|---|---|---|
| | | -1 | 0 | 1 |
| Reaction time (min) | $X_1$ | 60 | 105 | 150 |
| Reaction Temperature (°C) | $X_2$ - | 40 | 60 | 80 |
| Methanol-oil molar ratio (X) | $X_3$ | 3 | 9 | 15 |
| Catalyst Concentration (wt%) | $X_4$ | 1 | 3 | 5 |

## 2.5 Biodiesel Production

Each run of transesterification reaction of Used Vegetable Oil (UVO) with the calcined fused cockle shell-watermelon peels catalyst was conducted in a three-necked, 250mL Erlenmeyen flask outfitted with a thermometer and reflux condenser. An amount of measured Used Vegetable oil (UVO) were heated to their respective run temperatures as specified by table 1 using magnetic hot-plate stirrers. Based on experimental design, the heated oil was mixed with a corresponding amount of methanol. Subsequently, the mixture of heterogeneous catalysts was introduced into the reactor, and the reaction was left to proceed for the duration of the designated time. After completion, the reactions mixture was cooled and decanted (for phase separation), allowing separation of glycerol via gravity. The layers (glycerol, methyl ester, and catalyst) were further separated. In a separating funnel, the remaining liquid separated overnight. The upper layer, which contained unreacted methanol and biodiesel, was subsequently separated from the base layer., which contained glycerol and some residual solid catalyst. To eliminate excess catalyst, methanol, and glycerol from the recovered biodiesel, it was washed thrice with warm distilled water. Further drying was performed to remove any remaining moisture from the biodiesel. Afterwards, it was placed in a bottle and kept for characterization purposes. Fuel characterization of the biodiesel produced was conducted to assess its physicochemical qualities in accordance with applicable ASTM standards.
The resulting yield was analyzed using equation (2);

$$\text{Percentage of biodiesel yield} = \frac{\text{weight of biodiesel produced}}{\text{weight of oil}} \times 100 \tag{2}$$

## 3. Results and Discussion

### 3.1 Characterization of catalyst

*i.**Surface Morphology and Elemental Composition analysis (SEM-EDS analysis)***

The morphological characteristics of the precursor feedstocks and synthesized fused catalyst are depicted in the SEM images provided in Figure 1. The watermelon peel has a highly irregular porous structure and a heterogeneous fiber-bundled appearance due to its significant structural alteration. The observed spongy nature is a result of the calcination-induced sintering of tiny mineral aggregates and flocculated particles, and is therefore indicative of activation and catalysis-accessible surface area [23].

Figure 1b illustrates the rough surface, uneven and compactly formed particles collected into mass, and overall bulky appearance of cockle shells. A non-uniform structure of the particle size distribution is seen in (Figure 1c) for produced fused catalysts, which typically consists of the development of smaller aggregates of varied morphologies. Ash samples of used banana peels have been observed to have similar morphological findings(Betiku et al., 2016b), and also watermelon rind [24]. Identical pore micro properties were noted by [25] for cockle shell-based heterogeneous catalysts,[26] observed identical characteristics while producing Cao using waste seashells as the source of $CaCO_3$.Clusters of Ni-Cao particles may occur during preparation and calcination of metal impregnated catalysts, which could account for the irregular morphology. During the production of the catalyst, noticed a surface irregularity and particle size dispersion, comparable to that shown in fig 1c, and they characterized it as the outcome of the two waste materials' particle size structures combining during the catalyst synthesis.

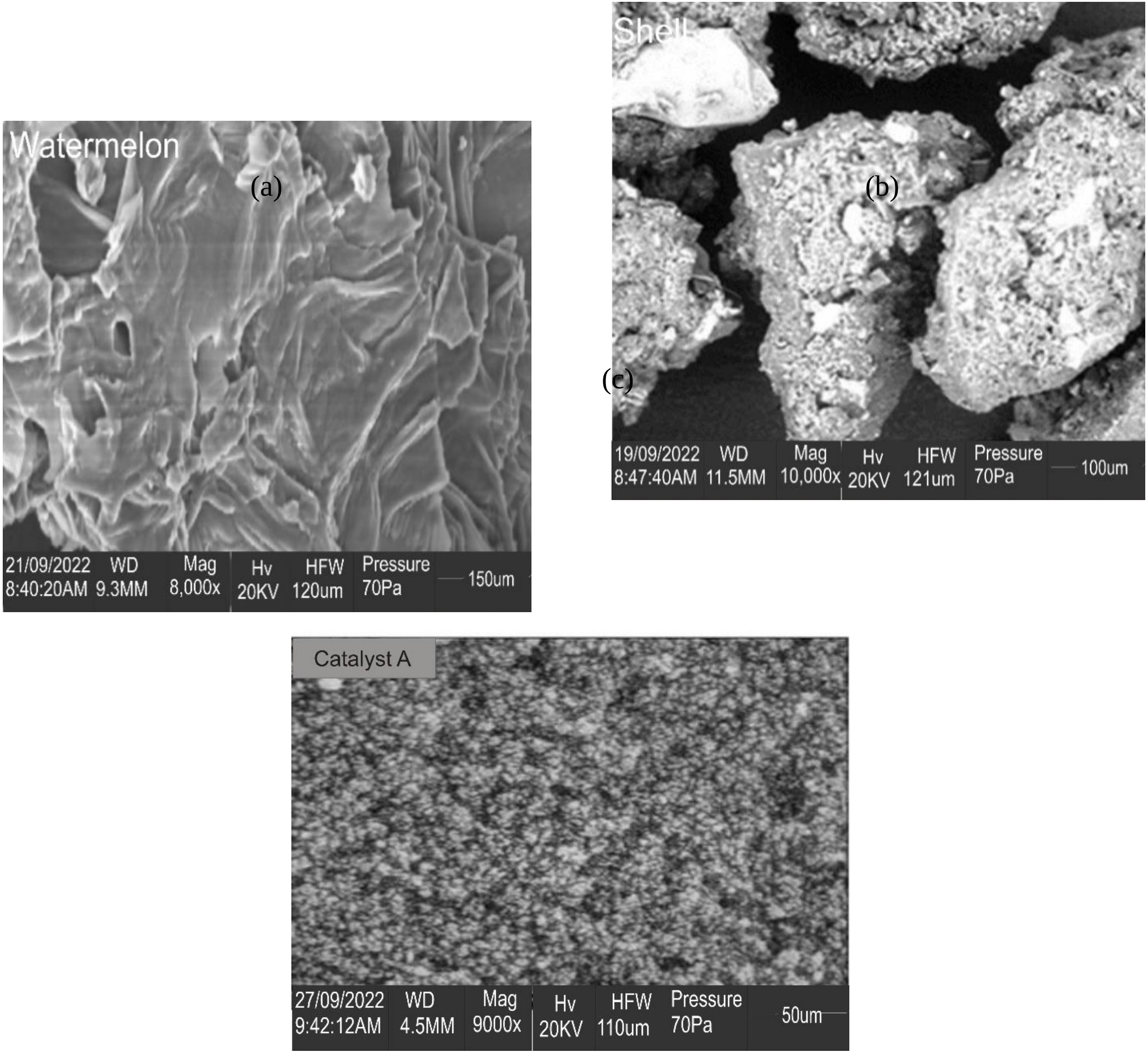


Figure 1. SEM analysis – a (watermelon peels), b (cockle shell), c (composite catalyst) (a) x150 (b) x100 (c) x50

Eds analysis, as given in table 2, determined the the catalyst's elemental composition and shows the elements present such as Na, k, Ca, S, O, Si, Fe, Ni etc. The composite catalyst's alkaline (calcium, potassium) and acidic (silicon, nickel) constituents indicate bifunctionality. This implies the catalyst can concurrently catalyze transesterification and esterification reactions. In [27]investigation of heterogenous catalyst developed from *Sesamum indicum* plant, the inclusion of calcium, potassium, and silicon boosted the catalyst's activity.[11] observed a similar observation for ripe plantain peels, as well as for calcined eggshell and pawpaw peels composite catalyst [28].

Table 2: Elemental composition of cockle shell, watermelon peels and composite catalyst**.**

| **Element Name** | **Element symbol** | **Weight percent** | | |
|---|---|---|---|---|
| | | **Cockle shell** | **Watermelon peels** | **Composite Catalyst** |
| Nickel | Ni | 0 | 0 | 5.3 |
| Calcium | Ca | 59 | 2.75 | 4.3 |
| Phosphorus | P | 3 | 3.68 | 1.23 |
| Nitrogen | N | 3 | 6.3 | 0.43 |
| Sulfur | S | 4.5 | 2.04 | 1.3 |
| Carbon | C | 8.5 | 65.28 | 25.4 |
| Potassium | K | 0 | 10.12 | 5.2 |
| Silicon | Si | 10 | 0.2 | 23 |
| Oxygen | O | 10 | 9.2 | 33.51 |
| Iron | Fe | 2 | 0 | 0 |
| Sodium | Na | 0 | 0.43 | 0.33 |

### *ii. XRD analysis*

Intensity peaks at 22°, 25°, 29°, 30°, 32°, 36°, and 49°, 68° in the X-ray diffraction spectra of the synthesized fused catalyst indicate the cubic Cao phase formed from cockle shells.[29] and [25] generated catalysts with comparable peaks, indicating that Cao was the predominate oxide. Similar to the finding reported in the work of [30], who characterized the Musa balbisiana peel-derived catalyst, these X-ray diffraction spectra showed weakly-intensified peaks at 2Ө values of 37.0°, 43.0°, and 62.5°, representing the presence of $K_2CO_3$, alongside the presence of $k_20$, as shown by the peaks at 2Ө values of 26.71.

In the case of the 2Ө values for 21.39, 25.78, and 72.78, the spectra indicated the availability of $SiO_2$ as a catalytic component. Catalysts for biodiesel synthesis using calcined wood ash and M. balbisiana underground stem were also discovered to contain $SiO_2$ [31], [32].

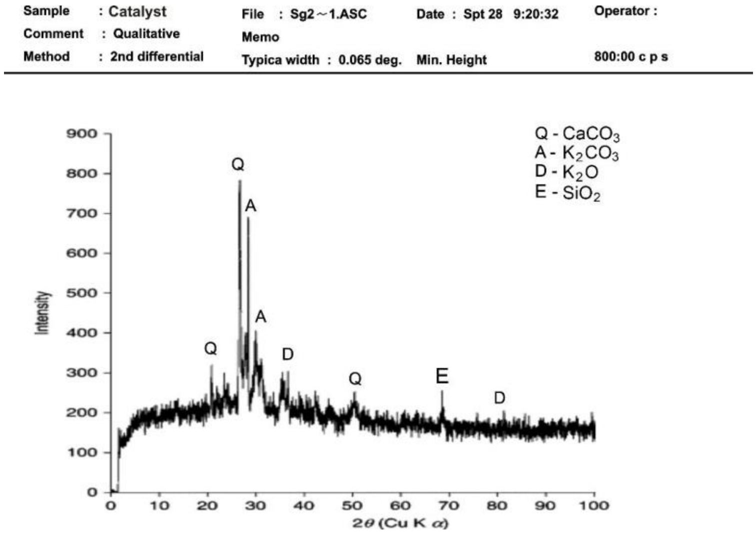


Figure 2. XRD ANALYSIS

### *Iii Textural Characteristics (BET analysis)*

The catalytic activity of any given solid base heterogeneous catalyst has a significant degree of dependence on its surface area, porosity, and mineral content. The BET characterization technique (surface area) and the BJH desorption summary (pore size and pore volume) were utilized to characterize the composite catalyst with the intent of ascertaining the effectiveness of the calcination procedure. Based on the results of the BET analysis, it was determined that the developed fused catalyst possess a surface area of 105.350 $m^2/g$. Additionally, the pore volume and pore size were determined as 0.60$cm^3/g$, 30.32A respectively. In comparison to other solid catalyst reported as shown in table 3, the synthesized catalyst displayed a high surface area and this is attributable to the process of size-reduction and sieving that was carried out. These results therefore show that the catalyst's external surface possesses the active site. Due to the larger pore size, it can improve diffusion problems, resulting in better flow channels. In the reaction mixture, this could expedite the rate of interaction between the material and the alcohol, thereby accelerating the reaction.

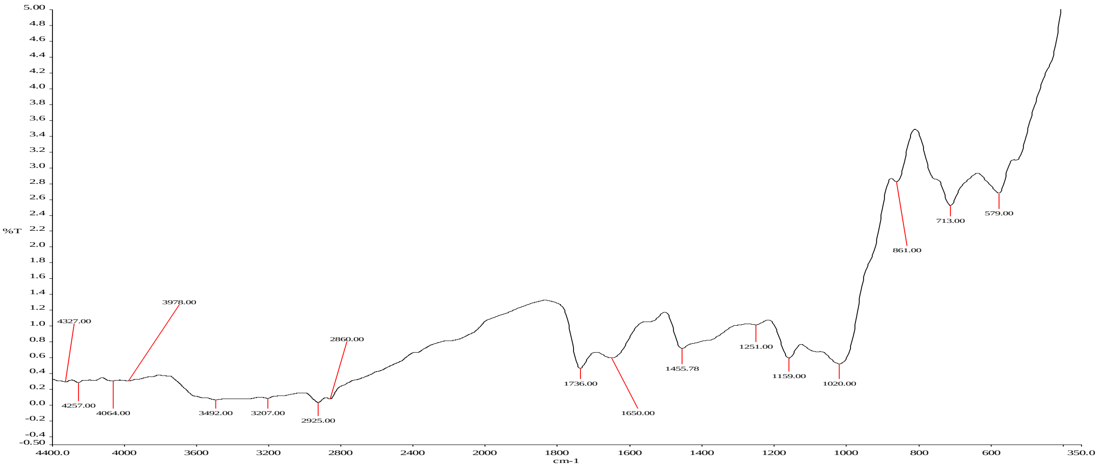
Table 3. Textural characteristics of catalyst

| CATALYST | Surface area | Pore Volume | Reference |
|---|---|---|---|
| Active razor shell | 85.27$m^2/g$ | 0.423cc/g | [29] |
| Chicken eggshells | 54.6 $m^2/g$ | 0.0218 $cm^3/g$ | [13] |
| Banana peels | 4.442 $m^2/g$ | 0.020$cm^3/g$ | [33] |

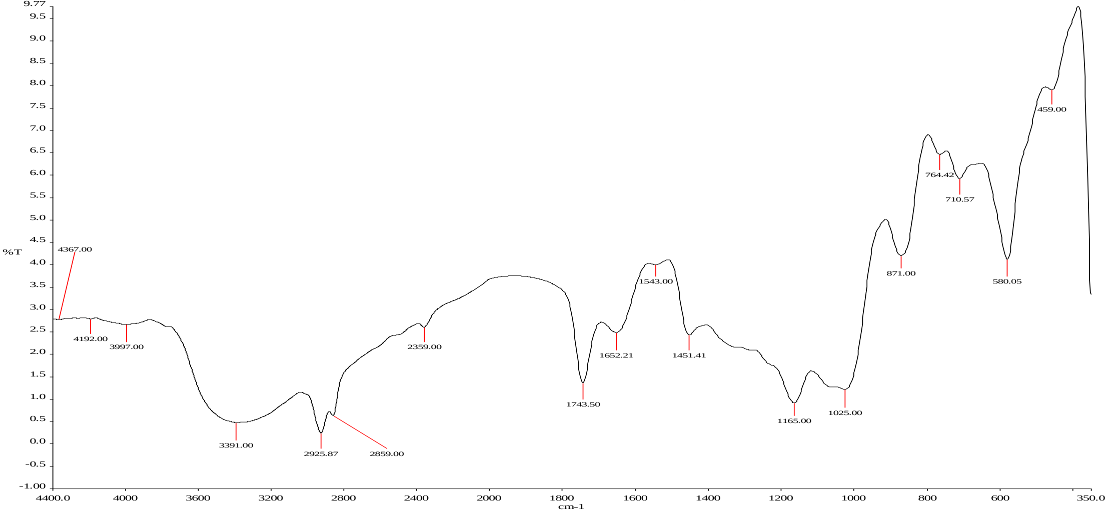
### *Iv Fourier Transform infrared spectroscopy (FTIR) analysis*

The spectroscopic technique of Fourier transform infrared spectroscopy was employed to determine the bond vibrations in the sample. Significant peaks were seen in watermelon peels at 4010$cm^{-1}$, 3500$cm^{-1}$, 3000$cm^{-1}$, 1850$cm^{-1}$, 1500$cm^{-1}$. Watermelon peels' FT-IR spectra are depicted in figure 3a. The weak bands observed in fig at 3200−3500$cm^{−1}$ are ascribed to the strong H−OH stretch or Si−OH, while bands at 1650, 1455.78, 1251, and 1159 $cm^{−1}$ are ascribed to carbonate C-O stretching and bending vibrations, which serve as a detectable characteristic of carbonate. According to the observations of [34], the vibration of hydroxyl groups and C0, respectively, was responsible for the formation of peaks at 3570 - 3420 $cm^{-1}$ and 1640 - 873 $cm^{-1}$. The 900 -$cm^{-1}$ peak is also influenced by symmetric and asymmetric stretching vibration bands in Si-O-Si.

Cockle shell catalyst FTIR spectra (Figure 3b) shows two $CaCO_3$ peaks at 711 $cm^{-1}$ and 846-880 $cm^{-1}$ which is attributed to carbonate ion ($Co_3^{2-)}$ stretching vibration. At 3638$cm^{-1}$, a distinct OH stretching band related to water physisorbed on Cao's surface also begins to show. Observing peaks at 3641$cm^{-1}$ when heterogeneous catalysts are synthesized from anadaragranosa shell [35], work supports our findings. Similar findings were reported by [36], who established that the peaks at 3400 cm-1 were due to the OH group in $Ca(OH)_2$.



(a)



(b)

Figure 3. FTIR spectra for calcined watermelon peels (a) and cockle shell (b)

### 3.2 Statistical Analysis and Experimental Design

Used vegetable oil transesterification process was analyzed using the Response Surface Methodology to determine the impact of varying temperature, methanol-oil ratio, reaction time, and catalyst concentration. The process of transesterification was modeled and optimized using the BBD with three factors and three levels. Twenty-nine experimental runs with a single response were produced. ANOVA was used to establish the models’ significance, and table 4 presents the findings of this study. The F-value helps determine the significance of the parameters' regression coefficient. The model is statistically significant with an F-value of 29.53 and a P-value of < 0.0001. Such a high F-value could only have occurred owing to noise if the probability was 0.01%. The findings showed a statistically significant relationship between all model terms, with the exception of the single term for the effect of reaction time, the term for the interaction between the methanol-oil ratio and time, and the terms for the interaction between catalyst and reaction time. Among other aspects, the biodiesel yield was most affected by the reaction temperature, thus, resulting in a larger coefficient.

The empirical model that shows the link between the process variable and the % biodiesel yield in terms of actual components utilizing multiple regression analysis, is as follows:

$$Y_1 = 45.37 - 0.73A + 2.25B + 0.14C - 4.86D + 0.0029AB - 0.0013AC + 0.0041AD - 0.059BC - 0.088BD + 0.36\,CD + 0.0027A^2 - 0.013B^2 + 0.15C^2 + 0.83D^2 \quad (3)$$

Where;
$Y_1$ is UVO biodiesel yield, A is Reaction time, B is Temperature, C is methanol-to-oil molar ratio, D is catalyst dosage (wt%).

Figure 4 represents the interaction between the actual experimental results and the predicted values. Within the intended range, the model and experimental results fitted reasonably.

**Table 4: ANOVA for quadratic model**

| **Source** | **Sum of Squares** | **Df** | **Mean Square** | **F-value** | **P-value** |
|---|---|---|---|---|---|
| **Model** | 1436.63 | 14 | 102.62 | 29.53 | <0.0001 Significant |
| A-Reaction time | 12.59 | 1 | 12.59 | 3.62 | 0.0778 |
| B- Temperature | 199.84 | 1 | 199.84 | 57.51 | <0.0001 |
| C- Methanol/oil ratio | 50.55 | 1 | 50.55 | 14.55 | 0.0019 |
| D- Catalyst concentration | 103.19 | 1 | 103.19 | 29.7 | <0.0001 |
| AB | 27.56 | 1 | 27.56 | 7.93 | 0.0137 |
| AC | 0.483 | 1 | 0.483 | 0.193 | 0.7149 |
| AD | 0.5476 | 1 | 0.5476 | 0.1576 | 0.6974 |
| BC | 199.09 | 1 | 199.09 | 57.29 | <0.0001 |
| BD | 49.91 | 1 | 49.91 | 14.36 | 0.002 |
| CD | 75.34 | 1 | 75.34 | 21.68 | 0.0004 |
| $A^2$ | 200.13 | 1 | 200.13 | 57.59 | <0.0001 |
| $B^2$ | 175.76 | 1 | 175.76 | 50.58 | <0.0001 |
| $C^2$ | 200.49 | 1 | 200.49 | 57.69 | <0.0001 |
| $D^2$ | 72.34 | 1 | 72.34 | 20.82 | 0.0004 |
| Residual | 48.65 | 14 | 3.48 | | |
| Lack of Fit | 43.41 | 10 | 4.34 | 3.31 | 0.1299 not significant |
| Pure Error | 5.24 | 4 | 1.31 | | |
| **Cor Total** | 1485.28 | 28 | | | |

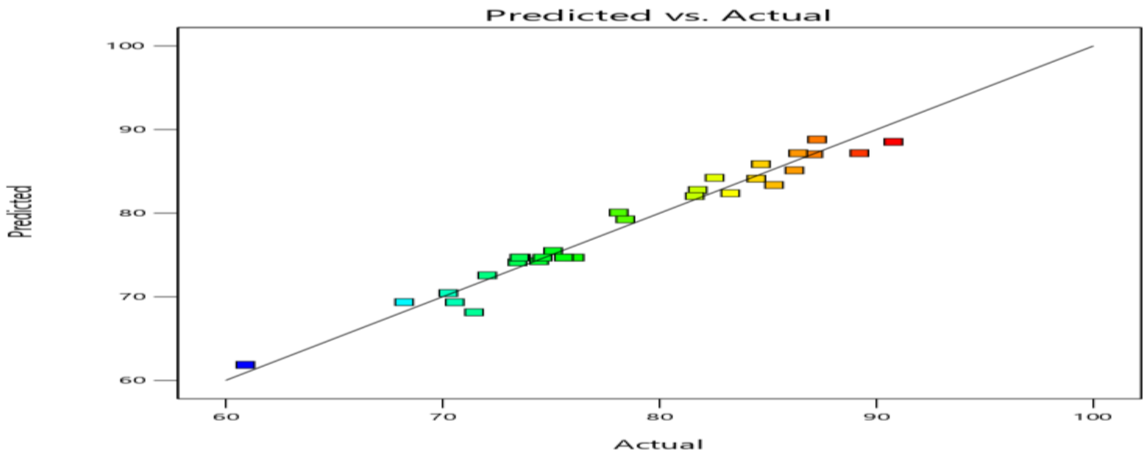


**Figure 4. Actual vs Predicted yield of biodiesel**

## 3.3 Optimization of variables Affecting Biodiesel yield

### 3.3.1 Impact of Catalyst concentration and Methanol-oil-molar ratio on biodiesel yield

The result shown in (Figure 5a) depicts the impact of methanol-oil molar ratio and catalyst concentration on biodiesel yield. From the figure, the amount of biodiesel produced rises in proportion to the amount of catalyst concentration present in the reaction. This result demonstarates that the yield increases as the catalyst concentrations increase at a high alcohol to oil molar ratio. The rate of increasing biodiesel yield changes slowly as the concentration of the catalyst gradually decreases at the other alcohol molar ratio. The biodiesel yield was low at low catalyst concentration (1-2wt%) and lower methanol contents (3-6), this can be attributable to the presence of few active sites and an inadequate amount of methanol necessary for the process wherein triglycerides are converted into methyl esters. Similarly [37], observed same trend when *Musa acuminata* pendicule was utilized for biodiesel production.

### 3.3.2 Impact of Catalyst Concentration and Reaction time on biodiesel yield

Figure 5b depicts the response for the interacting factors of catalyst concentration and reaction time. Biodiesel yield was shown to increase with both increased catalyst concentration and reaction time. However, with excess catalyst addition, the yield first increases and then decreases. This may be due to the viscosity of the reactant-catalyst mixture, which creates problems with mixing and hence inadequate reaction. Studies conducted by [38] on the transesterification of waste cooking oil to investigate the catalytic activity of KOH as both a homogeneous and heterogeneous catalyst for the synthesis of biodiesel found that similar trends emerged.

### 3.3.3 Impact of Reaction temperature and Reaction time on biodiesel yield

Figure 5c shows the surface plot of the UVO biodiesel yield as a function of reaction temperature and reaction time while the methanol-to-oil ratio and catalyst concentration was kept constant. The amount of biodiesel produced increases as both the temperature and the reaction time increase. According to the surface plots, maximum biodiesel yield was attained at the highest reaction temperature within the range of 50-70℃ and reaction time within the range of 100 – 130min. On increasing the temperature from 55 to 72℃ there was a tremendous increase in biodiesel yield at a corresponding value of 75.09% while at a reaction time within the range of 60- 110℃ there was an increase in yield but subsequent decrease at 110 to 150 ℃. In order to decrease the diffusion resistance of the oil, alcohol, and catalyst feedstock mixture, a higher temperature is preferred, since this will lead to a greater number of collisions between the reactant molecules [39]. In this study, biodiesel production was maximized at 63.34(91.8%). This result was consistent to those of [40]who noted a temperature of 65 °C was optimal for producing biodiesel with a of 91.2% from linseed oil using waste eggshell and pawpaw peel catalyst.

### 3.3.4 Impact of Methanol-oil-ratio and Reaction time on Biodiesel yield

The relationship of time and methanol-oil ratio on biodiesel yield is shown in fugre 5d. The amount of biodiesel produced steadily increases with time at low methanol-oil concentrations, while it decreases with time at high alcohol concentrations. Within the first 60–70 minutes of the process, the biodiesel production initially increases with the ratio of methanol to oil concentration, but subsequently begins to decrease. Due to the reversibility of the transesterification reaction by its very nature, suggests that the drop in biodiesel production that was observed could be related to the likely loss of fatty acids as the reaction is allowed to proceed for a significantly longer time period. Consistent trend comparable by [41] who reported the transesterification of sunflower oil. They attributed the decrease in yield with methanol-oil ratio rise to the prolonging of reaction to this time during transesterification reaction.

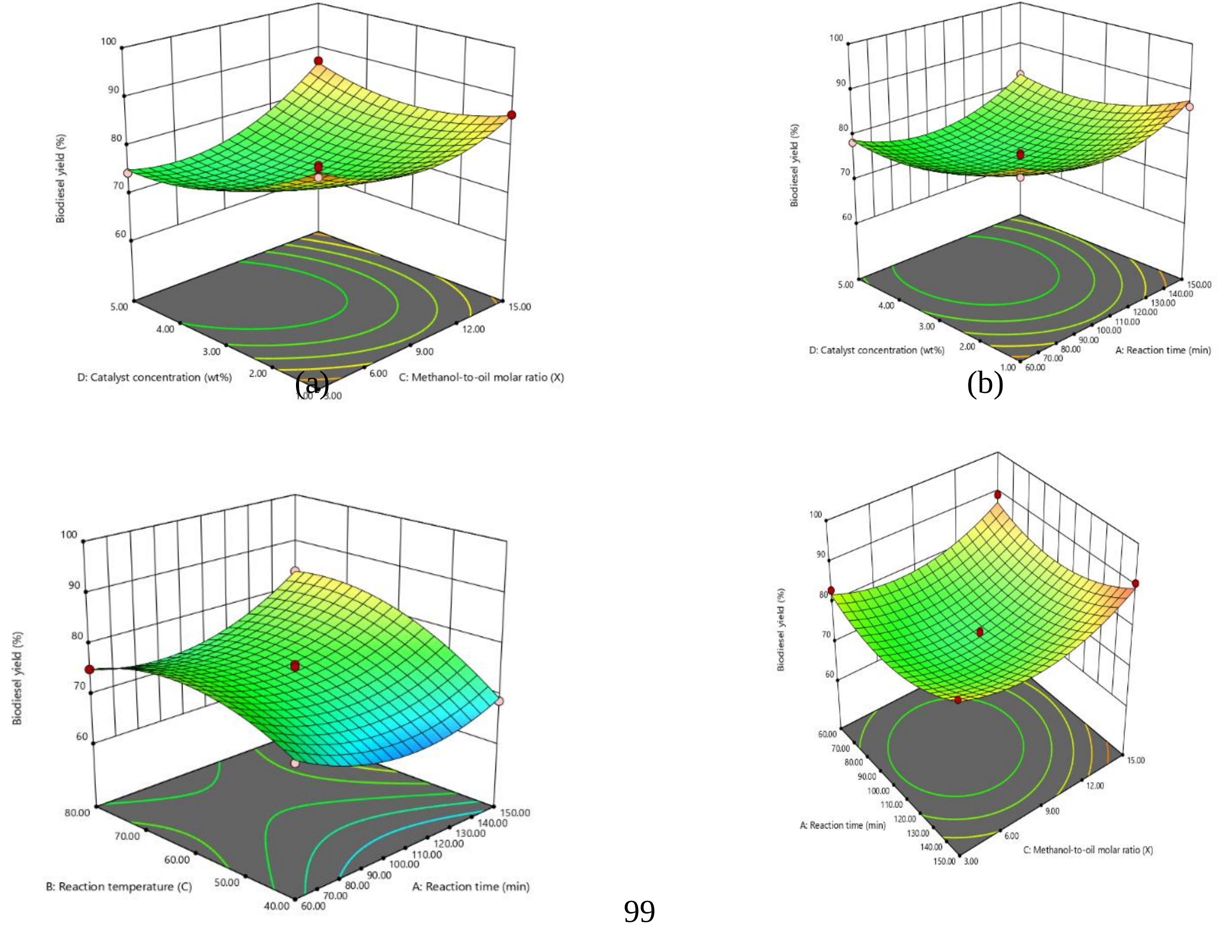
### 3.3.5 Impact of Methanol-oil-ratio and Reaction Temperature on Biodiesel

Figure 5e demonstrates the interaction between the methanol-oil molar ratio and reaction temperature with relation to the biodiesel yield at constant catalyst loading and reaction time. It can be deduced from the plot that the biodiesel yield increases with a subsequent increase in temperature towards 50.00ºC up to 9 mol/mol ratio and thereafter significantly decreases with both a drop in temperature and methanol-oil ratio content. The contour plot reveals that more than 82.85% of yield was produced between 3-9 mol alcohol and 50-60℃ temperature.

With an increase in temperature (70-80℃) comes a gradual decrease of the rate at which biodiesel production increases. This may be because methanol is vaporized at high temperatures, and the formation of methanol vapor bubbles lowers biodiesel output. However, at higher methanol-oil concentrations, yield decreases. This may be as aresult of high degree of soluble methanol in glycerol, and an increase in glycerol solubility leads to a difficulty in ester separation from aqueous layer [42]. Similar observations for the optimization of biodiesel production from used vegetable oil and eggshell ash were noted by [43]

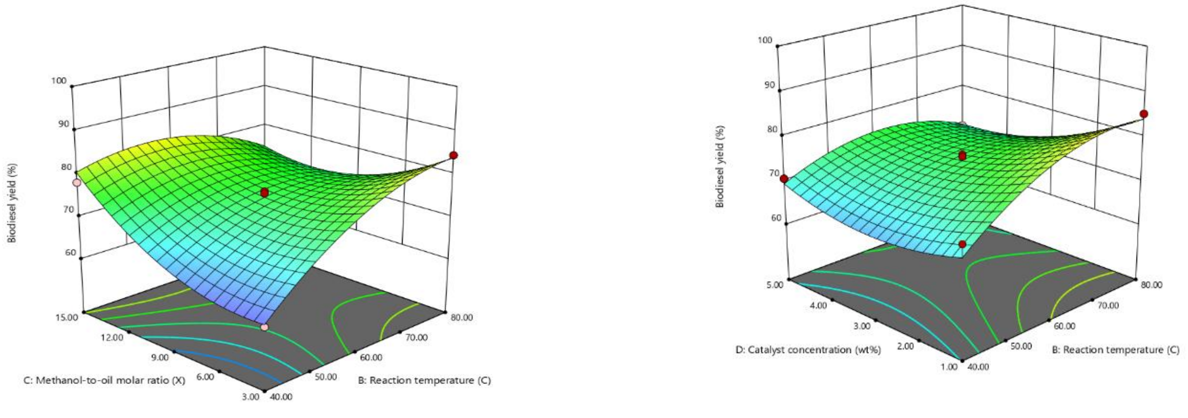
### *3.3.6* Impact of Catalyst concentration and Reaction temperature on biodiesel yield

Figure 5f displays the influence of temperature and catalyst concentration on biodiesel yield. With a relatively low concentration of the catalyst, the results demonstrate that an increase in temperature results in an increase in yield. This may be attributable to the transesterification process being expedited by more energy input, which increased the molecules' collision [44]. The rate of biodiesel yield increases as the temperature increases at intial point, achieving its maximal yield at intermediate amount of catalyst, and subsequently decreases at high catalyst concentration. This is the due to a negative temperature-concentration interaction as well as a negative quadratic concentration coefficient, likely resulting from soap formation side reactions. Similar results were obtained by [45] for the optimization of biodiesel production from mixture of edible and nonedible vegetable oil,



(a)

(b)



(e) (f)

Figure 5: 3D Representation showing the effect of Process parameters on Waste Vegetable oil biodiesel yield

A numerical optimization approach based on desired functions was employed to maximize the response (% biodiesel yield) from the UVO transesterification reaction. The goal of optimization is to identify the ideal conditions that maximize or minimize the process' response variable. Calcined fusion of cockleshells and watermelon peels promoted a transesterification reaction in which the most favorable conditions for biodiesel production were identified at a temperature of 63.34°C, catalyst concentration of 1.05 wt%, reaction time of 149.41 min and methanol / oil molar ratio of 14.45:1 with the predicted biodiesel yield of 91.77 wt%. The reliability of this condition was further confirmed by performing three other experiments, and a weighted average biodiesel yield of 91.92 wt% was determined for the procedure. As can be seen, the predicted yield and the actual yield from the experiment are in agreement. The optimized biodiesel production parameters are in some level of agreement those of prior studies.

### 3.4 Physicochemical Properties of Biodiesel

The biodiesel produced utilizing fused cockle shell-watermelon peels as catalyst for transesterification was compared to ASTM and EN standards as given in the table 4 and determined to be in compliance. The biodiesel from waste cockle shell and watermelon peels is darkish brown in colour with a pungent smoky smell. The acid value for biodiesel (0.39 mg KOH/g) is within the ASTM D6751 standard range (0.50max) and much lower than those for waste vegetable oil. An excessively high acid value is undesirable as it means the fuel is strongly acidic, which would corrode engine parts [46]. The density of biodiesel obtained was 836kg/m$^3$. Maintaining a density number within tolerable ranges is vital to ensure ideal air-to-fuel ratios necessary for complete combustion. Incomplete combustion and emissions of particulate matter are possible results of high-density biodiesel use. The calorific value is a method for determining the amount of heat energy contained in a fuel produced by a chemical reaction in the engine's combustion chamber. The biodiesel had a calorific value of 38.2Mj/kg. Higher calorific power translates into more fuel energy. Cetane number obtained is 48.7(< 51) EN14214 standards. The biodiesel's cetane number tells us whether or not it will spontaneously ignite when injected into the engine. It's important to note that a higher cetane number implies good combustion, which ultimately leads to greater efficiency of the engine motor. Fuel flammability is quantified by the flash point, which is inversely proportional to volatility. In the absence of a flame or spark, it depicts fuel's minimum operating temperature of which it can ignite spontaneously. High flash point increases handling and storage safety [47]. The samples' flashpoints are within ASTM D93 limits (min 130°C). This means the biodiesel sample can be safely handled. The less viscous biodiesel is, the simpler it is to pump it into an engine for atomization. The amount of moisture present in biodiesel has an effect that promotes an increase in acidity, which then leads to the formation of emulsion [48]. Hence a low moisture content is desirable. The moisture content which was attained was 1.5%. The moisture content was very low.

**Table 5. Physiochemical properties of Biodiesel**

| Property | Value | ASTMD6751 | EN14214 |
|---|---|---|---|
| Color | Light brown | Not specified | Not specified |
| Acid value (mg KOH/g) | 0.39 | ≤ 0.5 | ≤ 0.5 |
| Density (kg/m$^3$) | 836 | 860-900 | 850 |
| Calorific value (MJ/kg) | 38.2 | Not specified | ≥35 |
| Cetane Number | 48.7 | 55 | ≥47 |
| Flashpoint (°C) | 145.8 | 185 | ≥130 |
| Kinematic viscosity (mm$^2$/s) | 5.17 | 1.9-6 | 3.5-5 |
| Moisture content (%) | 0.015 | ≤0.03 | ≤0.02 |

## 4 Conclusion

This research examined the biodiesel synthesis from UVO utilizing a bi-component bio-waste heterogeneous catalyst obtained from the fusion of calcined cockle shells and watermelon peels. Cockle shell and watermelon peels was characterized and the synthesized catalyst's analysis revealed that calcium (4.3) and Potassium (5.2) were the catalysts' major active element, prominent for its catalytic activity. The characterized catalysts have demonstrated its capability of functioning as a sustainable feedstock for the production of biodiesel**.** The Box-Behnken approach was effectively utilized for the purposes of modeling and optimizing the transesterification process**.** At optimal process parameters of reaction duration of 149min, temperature of 63.34°C, catalyst concentration of 1.05 wt%, and methanol-to-oil ratio of 14.45, the optimal biodiesel yield of 91.77 was attained. The most influential variable that had a significant impact in determining the final yield was temperature, followed by the concentration of the catalyst and methanol-oil ratio. The qualities of biodiesel produced were determined to be compliant with biodiesel standards (ASTM D 6751, EN 14214), which indicates that it is suitable for use in the powering of internal combustion engines.

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